Dynamic Contact Angles

by Rossen Sedev

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UniSA
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For Particle and Material Interfaces

The Wark™

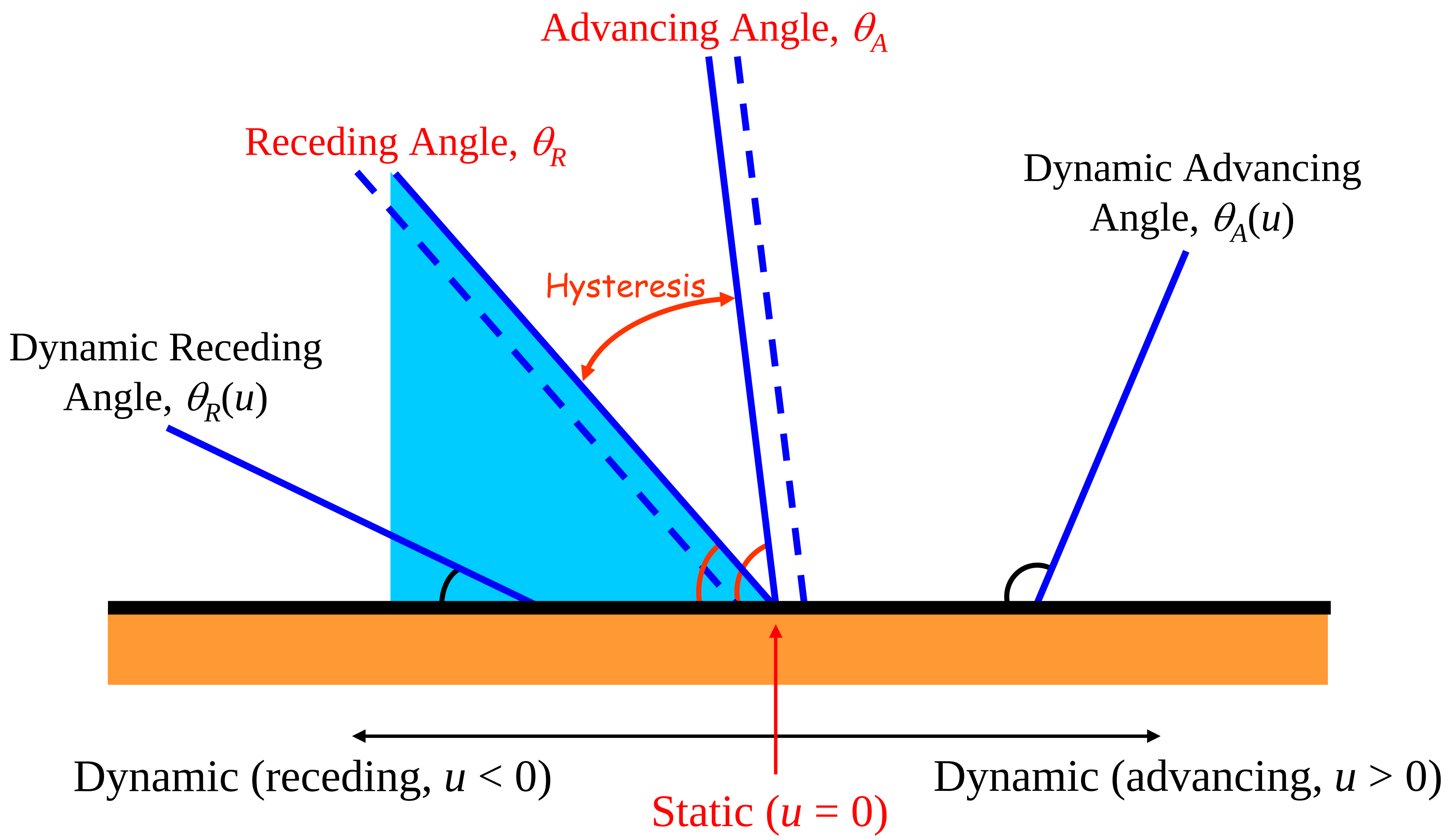
Outline

- **Dynamic Contact Angles**
  - Phenomenology
- **Theoretical Description**
  - Hydrodynamic Approach
  - Molecular-Kinetic Approach

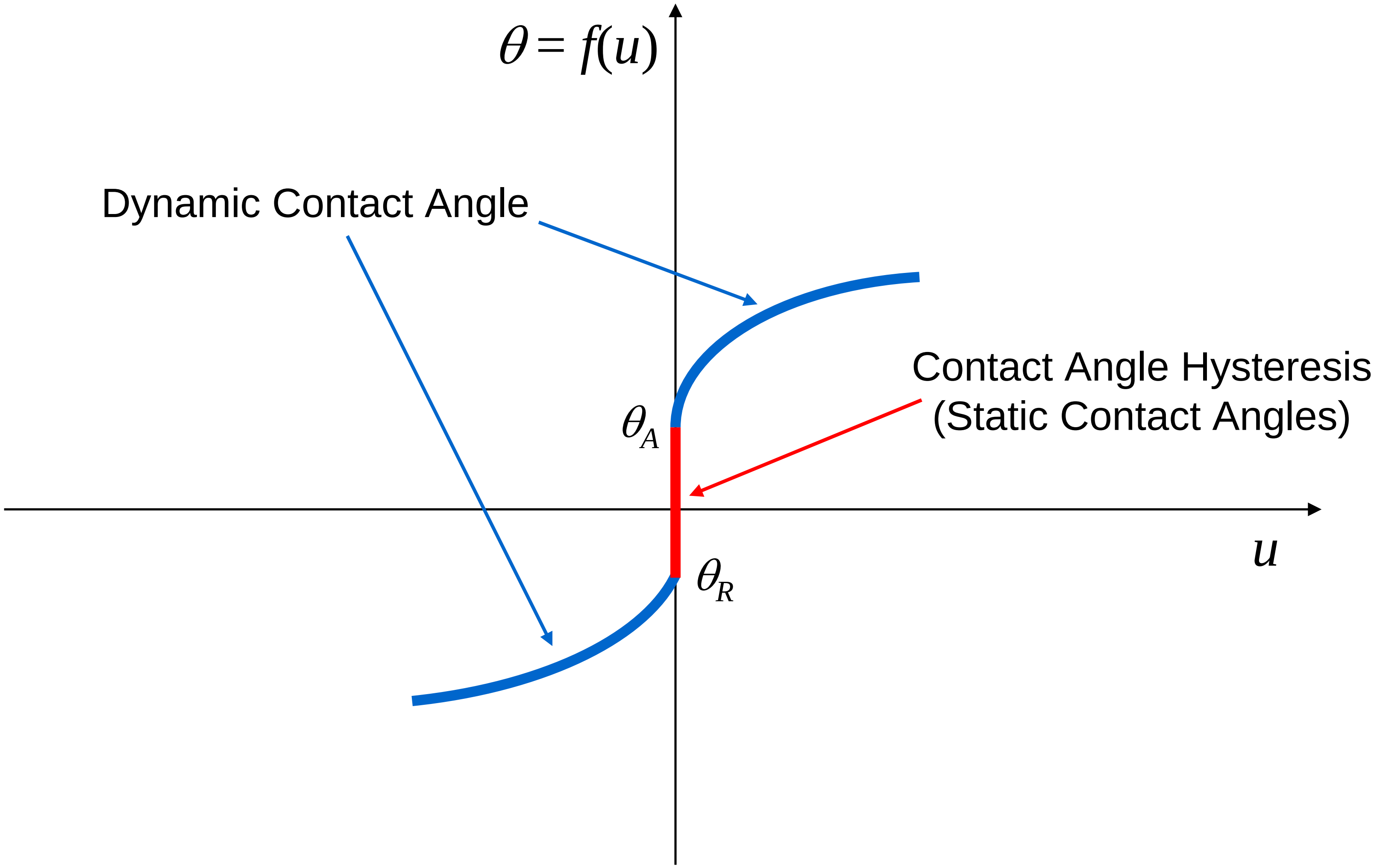
1. Phenomenology

- Moving Contact Line
- Quasistatic Wetting
- Maximum Speed of Wetting
- Dewetting

Contact Line: Static & Dynamic



Contact Angles: Static & Dynamic



Quasistatic Wetting (Very Low Speeds)

Experimental Observation:

At low contact line speed (~10 μm/s or less for water) the contact angle remains practically constant, i.e. quasistatic.

Hypotheses:

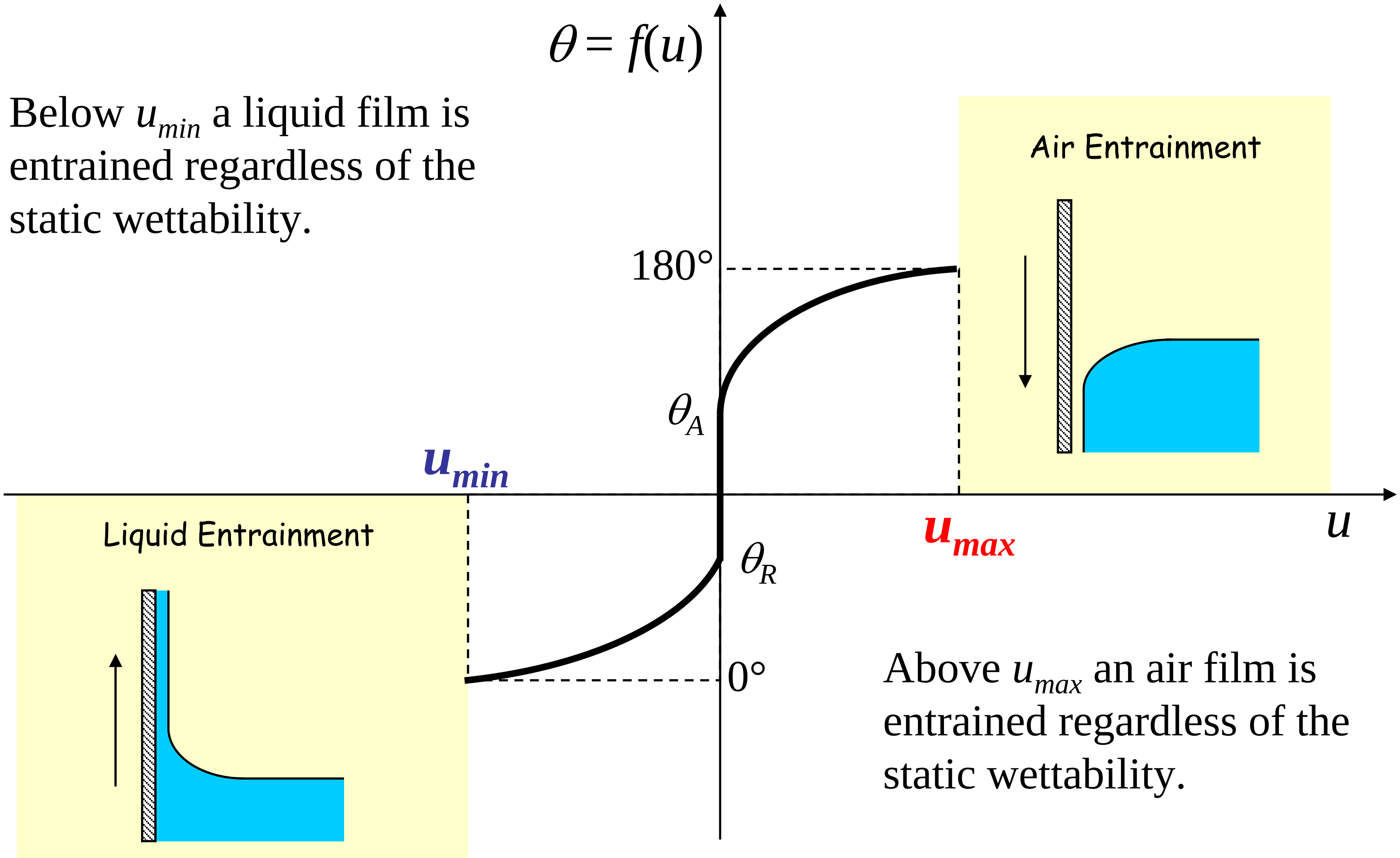
- The relaxation of the liquid molecules at the three-phase line is so fast that the movement is essentially quasi-static (Hansen & Miotto, 1957);
- The contact angle velocity dependence at low speed is so weak that it is within experimental error, i.e. cannot be detected (Sedev et al, 1993).

Practical Aspect:

- Often the contact angle dependence on the speed of wetting is unimportant at very low speeds but this must be checked;
- The advantage of advancing the liquid slowly over the surface is that a fresh surface is always exposed to the liquid (advancing contact angles);
- For receding contact angles the situation is more complicated and the influence of kinetic effects cannot be excluded *a priori*.

Film Entrainment (Very High Speeds)

Below u_{min} a liquid film is entrained regardless of the static wettability.



Above u_{max} an air film is entrained regardless of the static wettability.

Maximum Speed of Wetting

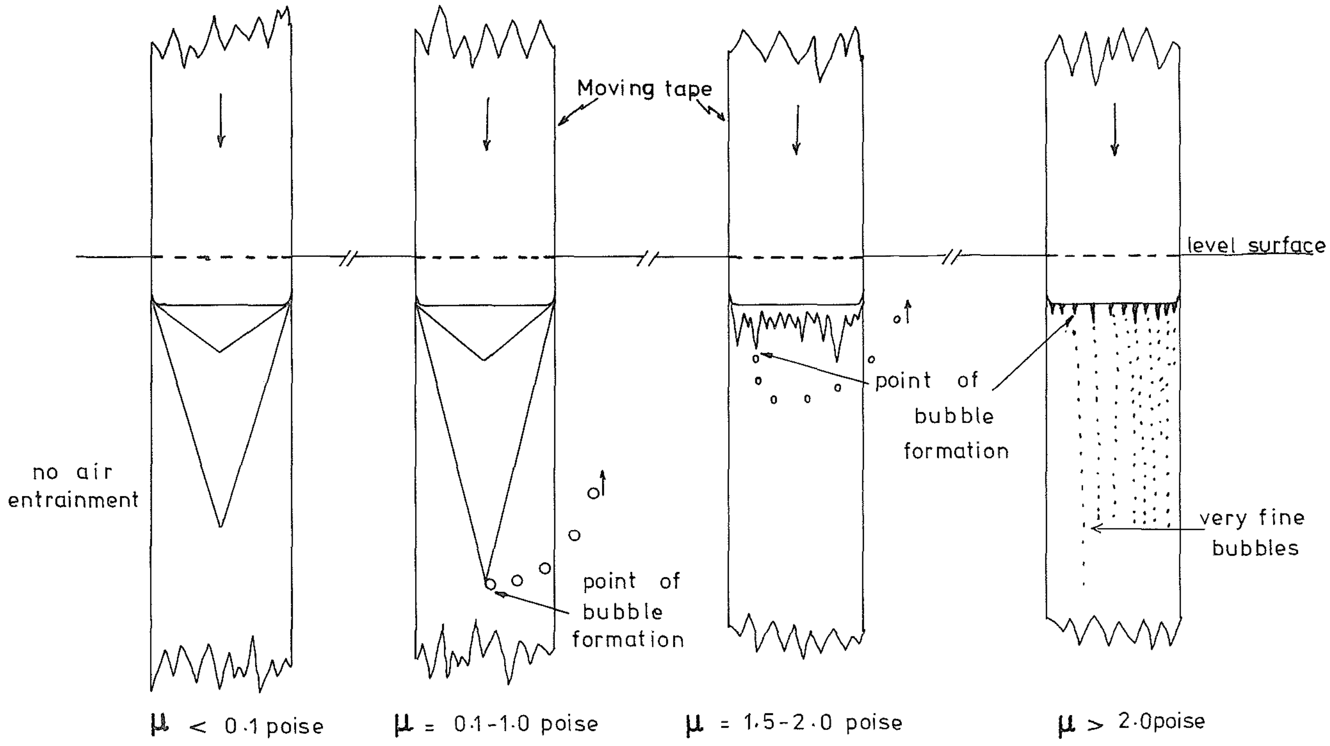
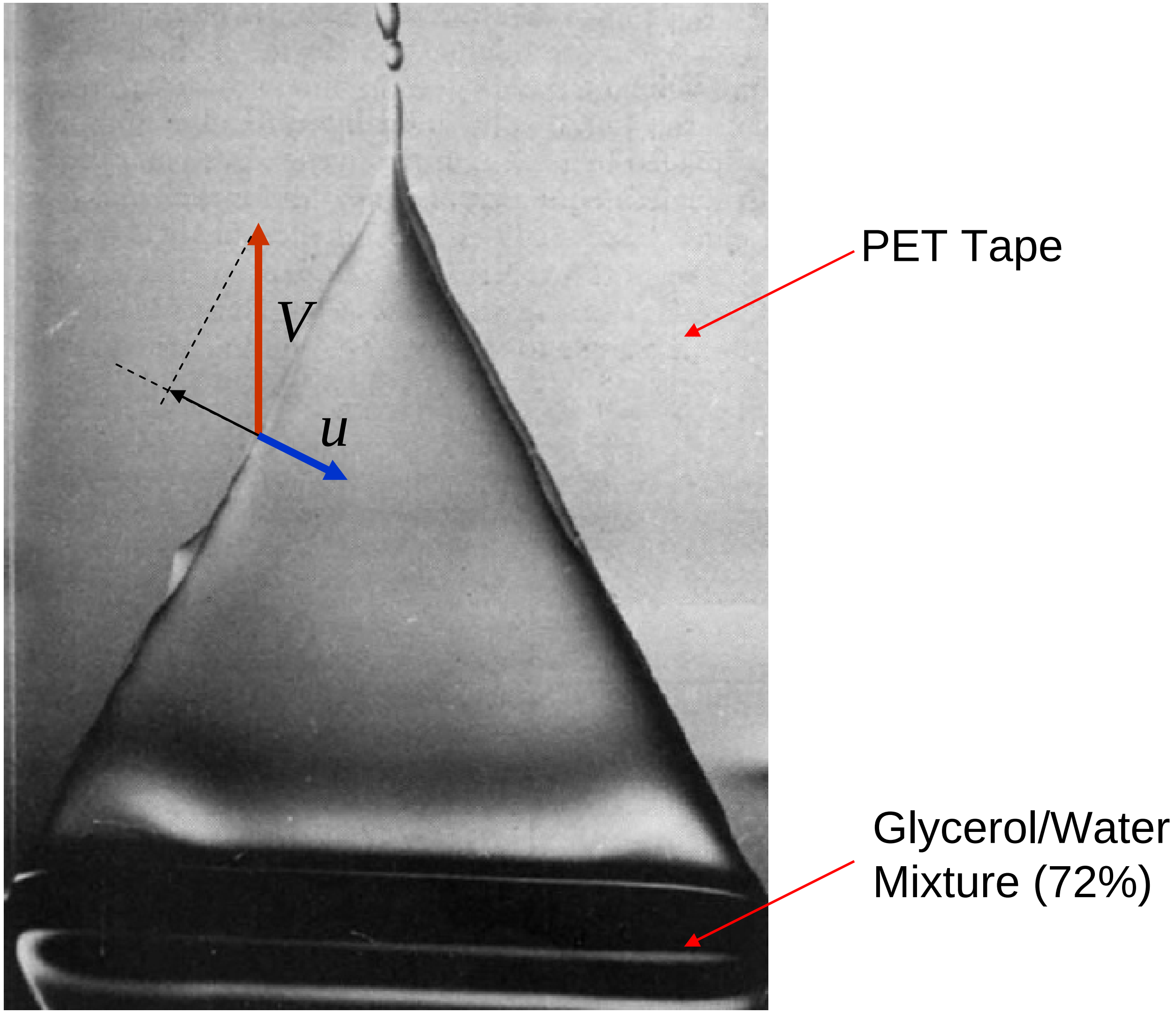


Fig. 2. Characteristic shape of the air intrusion and contact time as a function of fluid viscosity.

Burley & Kennedy (1978)

Maximum Speed of Dewetting



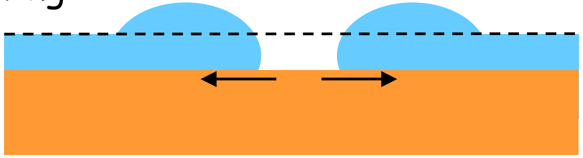
Blake & Ruschak (1979)

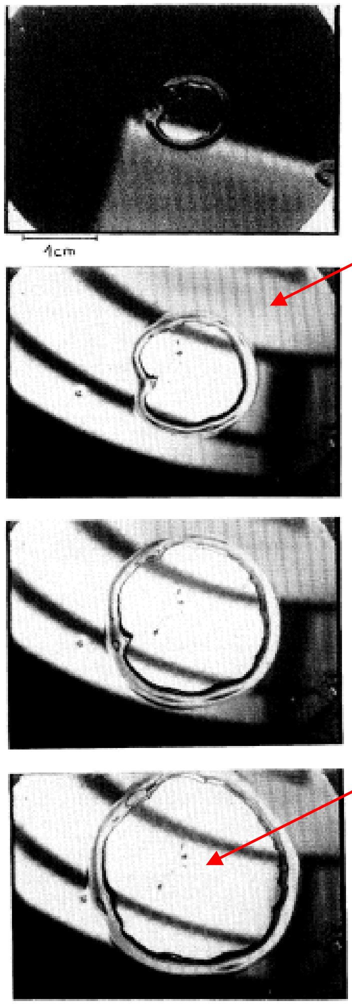
Dynamics of Dewetting

Metastable film:

Nucleation:

Dewetting:





PDMS Film (30 µm)

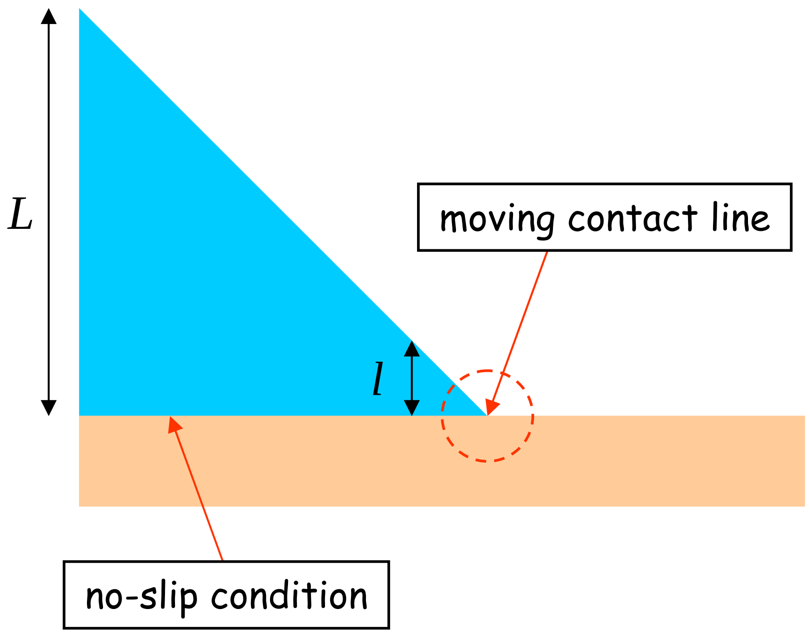
Fluoroalkylsilane coated Si wafer

Redon et al (1991)

2. Hydrodynamic Approach

- Driving Force
- Viscous Dissipation
- Voinov's Equation

Hydrodynamic Approach



Large scale (L):

- Continuous description, i.e. standard hydrodynamics (Navier-Stokes equations).

Small scale (l):

- Inconsistency when the macroscopic approach is extended up to the wall;
- Introduce a cut-off length which effectively encapsulates the peculiar phenomena occurring in the three-phase zone.

Energy dissipation is largely viscous, i.e. due to the friction between the liquid layers. Therefore the viscosity of the liquid plays a major role.
Viscous dissipation occurs in the bulk liquid, i.e. away from the contact line. Therefore (at least) two length scales must be specified.

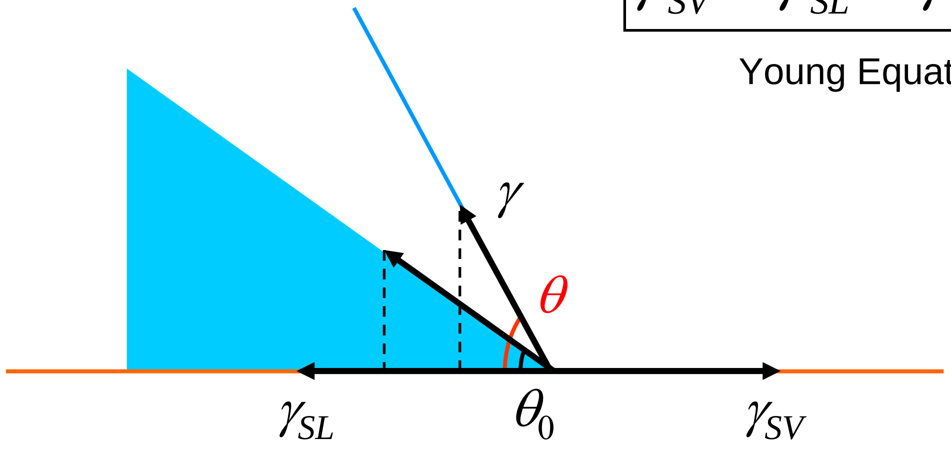
Driving Force

The unbalanced Young force, f_Y, is the driving force for the contact line:

$$f_Y = \sum \gamma_{ij} \cos \alpha_i$$

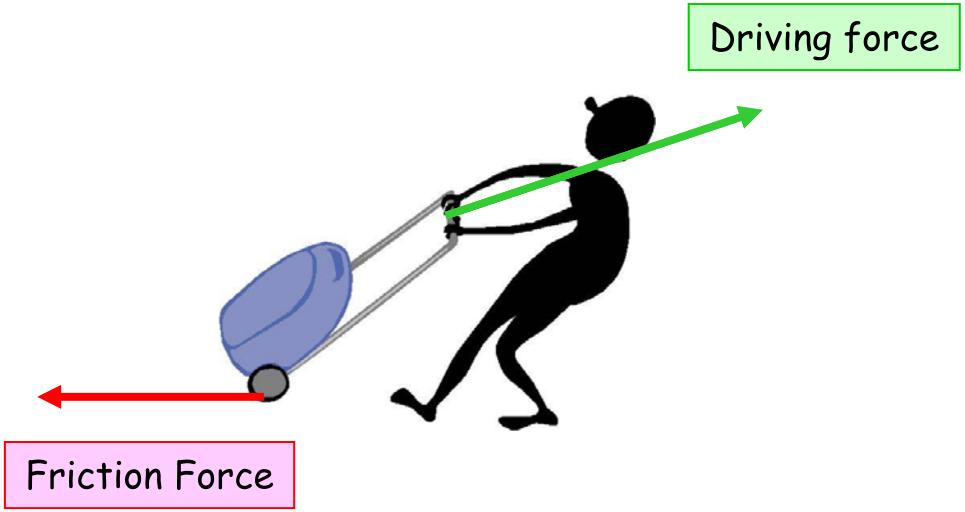
$$\gamma_{SV} - \gamma_{SL} = \gamma \cos \theta_0$$

Young Equation



$$f_Y = \gamma_{SV} - \gamma_{SL} - \gamma \cos \theta = \gamma \left(\cos \theta_0 - \cos \theta \right)$$

Viscous Dissipation



Power, P, is the rate at which work is done:

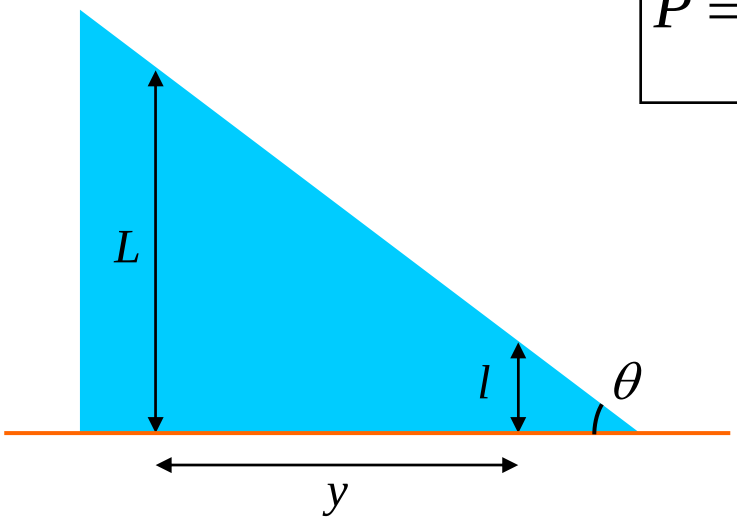
$$P \cong \frac{W}{t} \cong \frac{fx}{t} \cong fu$$

Rate of viscous dissipation is essentially power:

$$P = f_{\mu} u \approx \mu \frac{u}{x} yzu \approx \mu \frac{u}{x} xyz \frac{u}{x} \approx \mu V \left(\frac{u}{x} \right)^2$$

Rate of Viscous Dissipation

$$P = \mu V \left(\frac{u}{x} \right)^2$$



$$V \approx \frac{Ly}{2} \approx \frac{L^2}{2\theta}$$

$$P = \int \mu \left(\frac{du}{dx} \right)^2 dV \to 3 \frac{\mu u^2}{\theta} \ln \frac{L}{l}$$

Driving Force vs. Drag

$$\boxed{fu = P}$$

Driving Force: $$f = \gamma\left(\cos\theta_0 - \cos\theta\right) \xrightarrow{\theta \ll 1,\ \theta_0 = 0} \gamma\frac{\theta^2}{2}$$

Rate of Dissipation (Drag): $$P = 3\frac{\mu u^2}{\theta}\ln\frac{L}{l}$$

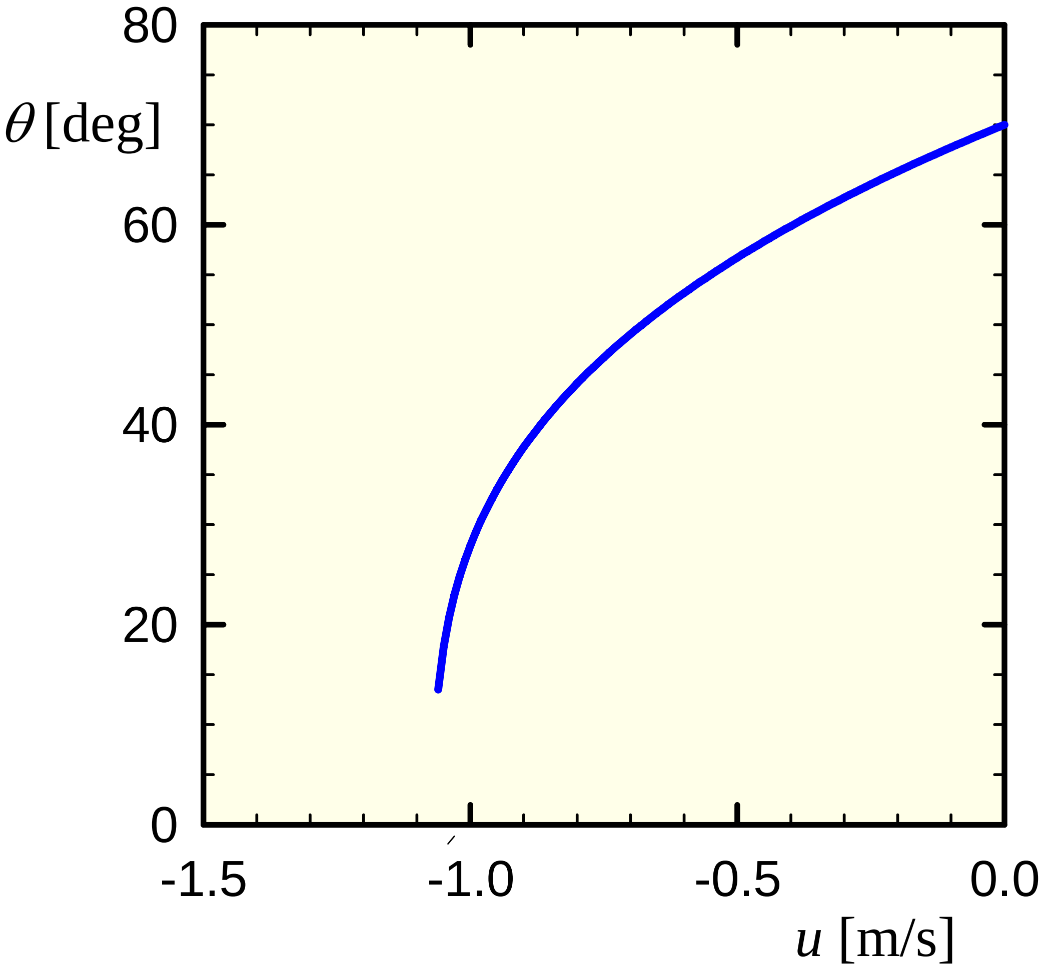
$$\boxed{\theta^3 = 6\frac{\mu u}{\gamma}\ln\frac{L}{l}}$$

$$\ln\frac{L}{l} \sim \ln\frac{1\ \text{mm}}{1\ \text{nm}} \approx 14$$

size of the meniscus (1 mm)

molecular size (1 nm)

Voinov's Equation



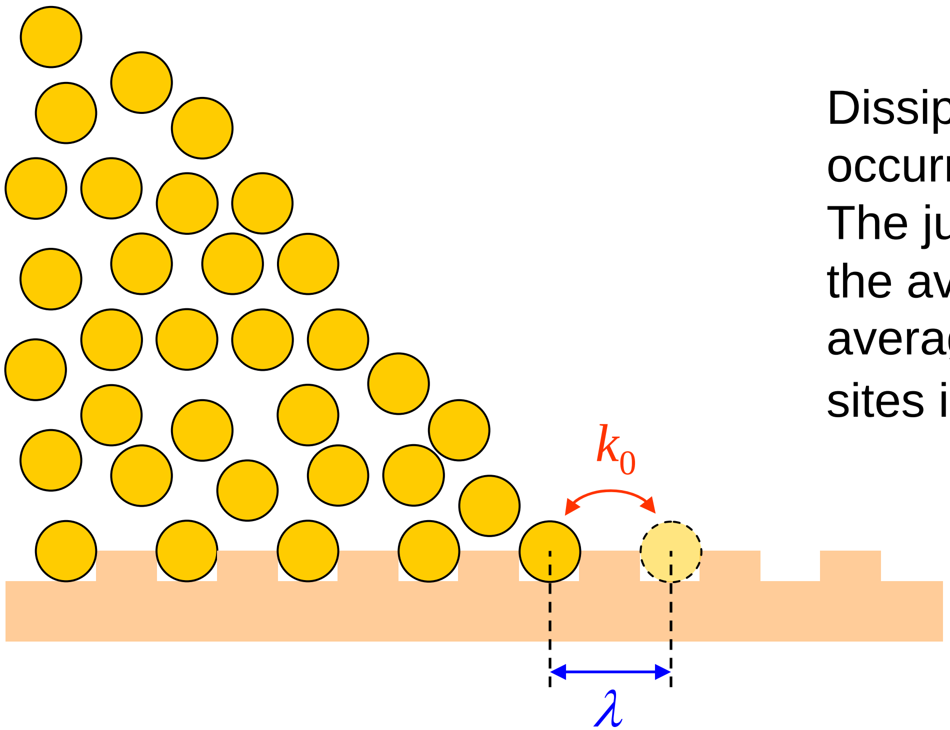
$$\theta^3 = \theta_0^3 + 9\frac{\mu u}{\gamma}\ln\frac{L}{l}$$

Voinov (1976)

3. Molecular Kinetic Approach

- Blake’s Theory
- Linearised Version
- Optimal Wettability for Coating

Microscopic Picture



Dissipation is mainly a molecular event occurring at the contact line.
The jump frequency at equilibrium is k_0; the average jump distance is λ and the average number density of adsorption sites is n.

$$n = \frac{N}{A} \cong \frac{1}{\lambda^2}$$

Driving force – the unbalanced Young force (a macroscopic expression);
Rate of dissipation – described by Eyring's rate theory.

$$k_0 = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_W}{k_B T} \right)$$

free energy of activation

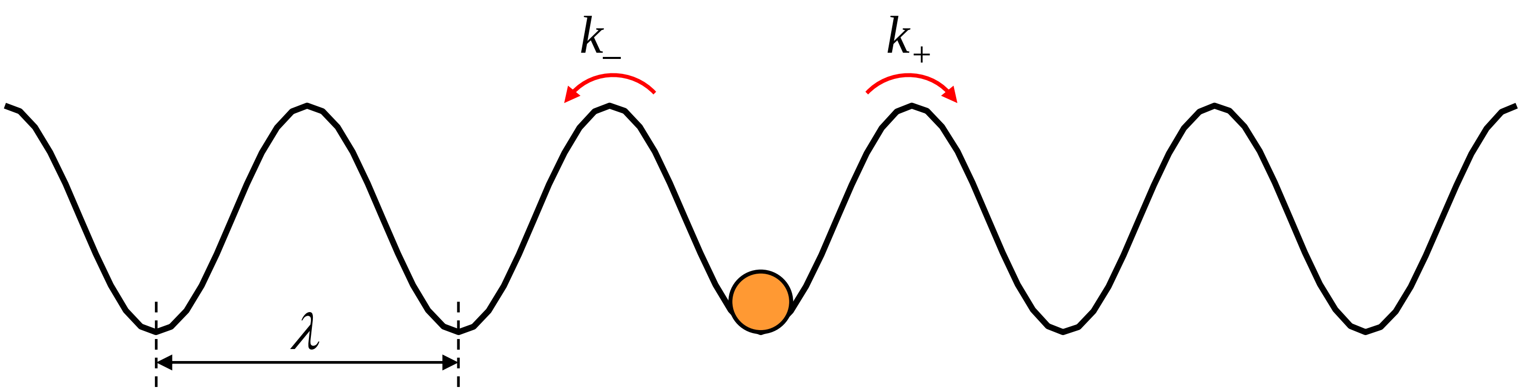
Static Contact Line

$$\boxed{f = 0}$$

Equilibrium Contact Angle

$$\boxed{k_+ = k_-}$$

Jumps left and right
are equally probable



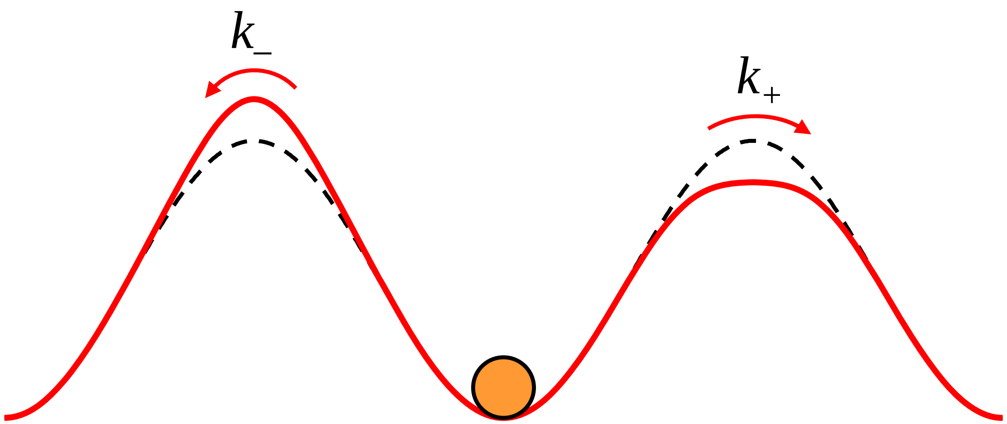
$$\boxed{u = \left(k_+ - k_-\right)\lambda = 0}$$

The contact line does not
move (on the average)

Dynamic Contact Line

$f > 0$ Dynamic Contact Angle (Advancing)

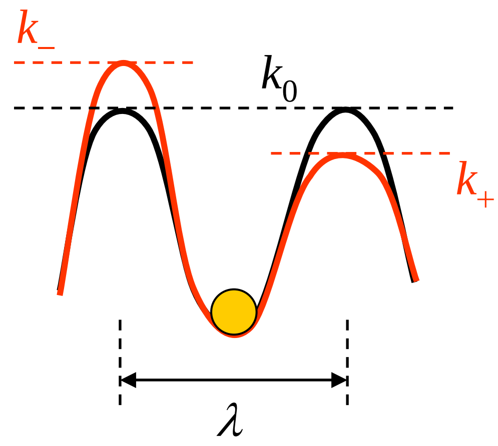
$k_+ > k_-$ Forward jumps are more probable



$u = (k_+ - k_-)\lambda > 0$ The contact line moves forwards (on the average)

Eyring’s Rate Theory

$$k_{\pm} = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_W \mp W}{k_B T} \right) = k_0 \exp\left(\pm \frac{W}{k_B T} \right)$$



$$u = (k_+ - k_-)\lambda = k_0 \left[\exp\left(\frac{W}{k_B T} \right) - \exp\left(-\frac{W}{k_B T} \right) \right] \lambda = 2 k_0 \lambda \sinh \frac{W}{k_B T}$$

Eyring's Theory of Viscosity

Viscous force (per molecule): $$f_\mu = \mu\lambda^2 \frac{u}{\lambda}$$

Alteration of the energy barrier: $$W = f_\mu \frac{\lambda}{2} = \frac{1}{2}\mu\lambda^2 u$$

$$u = 2k_0\lambda \sinh\frac{\mu\lambda^2 u}{2k_B T} \approx \mu u \frac{k_0\lambda^3}{k_B T}$$

$$\boxed{\mu = \frac{k_B T}{k_0\lambda^3} = \frac{h}{\lambda^3}\exp\left(\frac{\Delta G_\mu}{k_B T}\right)}$$

Blake's Theory (MK Theory)

driving force (per molecule):

$$f_D = f_Y \lambda = \gamma \left(\cos\theta_0 - \cos\theta \right) \lambda$$

Alteration of the activation barrier:

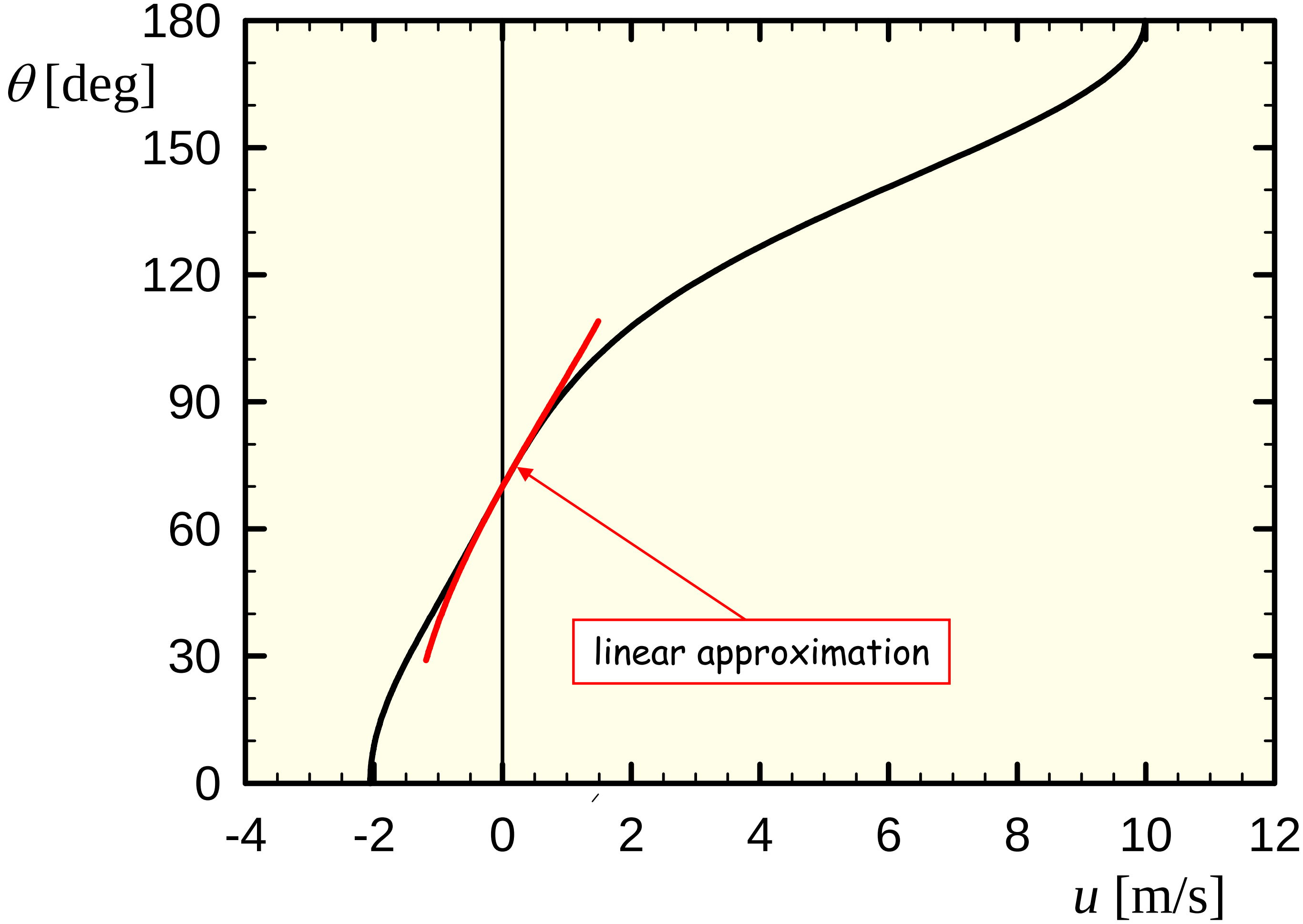
$$W = f_D \frac{\lambda}{2} = f_Y \frac{\lambda^2}{2}$$

$$u = 2k_0 \lambda \sinh \frac{W}{k_B T} = 2k_0 \lambda \sinh \frac{\gamma \left(\cos\theta_0 - \cos\theta \right) \lambda^2}{2k_B T}$$

$$\cos\theta = \cos\theta_0 - \frac{2k_B T}{\gamma \lambda^2} \sinh^{-1} \frac{u}{2k_0 \lambda}$$

Blake & Haynes (1969)

MK Theory: Full & Approximations



MK Theory: Linear Approximation

$$\sinh x \xrightarrow{x \to 0} x$$

$$u = 2k_0\lambda \sinh \frac{\gamma\left(\cos\theta_0 - \cos\theta\right)\lambda^2}{2k_B T} \to \frac{k_0\lambda^3}{k_B T}\gamma\left(\cos\theta_0 - \cos\theta\right)$$

$$u = af = \frac{1}{b} f$$

a – mobility [s/kg]
b – friction coefficient [kg/s]

B [Pa.s] represents contact line friction in the same fashion as μ [Pa.s] represents bulk (viscous) friction:

$$\boxed{B = \frac{k_B T}{k_0\lambda^3}}$$

MK Theory & Viscosity

$$k_0 = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_W}{k_B T} \right)$$

Split ΔG_W into viscous & surface components:

$$\boxed{\Delta G_W = \Delta G_\mu + \Delta G_S}$$

$$k_0 = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_\mu}{k_B T} \right) \exp\left(-\frac{\Delta G_S}{k_B T} \right)$$

$$\mu = \frac{h}{\lambda^3} \exp\left(\frac{\Delta G_\mu}{k_B T} \right), \qquad k_S = \frac{k_B T}{h} \exp\left(-\frac{\Delta G_S}{k_B T} \right)$$

$$\boxed{k_0 = \frac{h}{\mu \lambda^3} k_S}$$

MK Theory with Explicit Viscosity

$$u = \frac{2hk_S}{\mu\lambda^2}\sinh\frac{\gamma\left(\cos\theta_0 - \cos\theta\right)\lambda^2}{2k_BT}$$

Blake (1988)

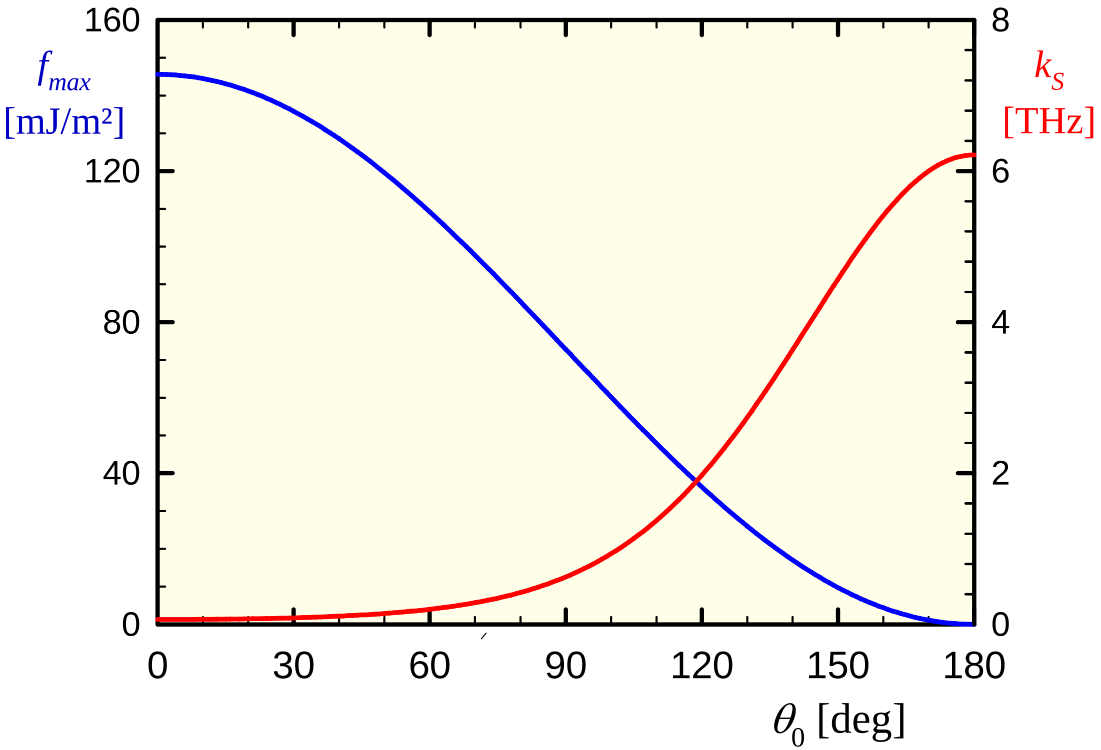
Linearised version: $$u = \frac{hk_S}{\mu k_BT}\gamma\left(\cos\theta_0 - \cos\theta\right)$$

$$B = \frac{\mu k_BT}{hk_S}$$

$$\frac{\mu u}{\gamma} = \frac{hk_S}{k_BT}\left(\cos\theta_0 - \cos\theta\right) \approx \frac{hk_S}{2k_BT}\left(\theta^2 - \theta_o^2\right)$$

MK Theory & Adhesion

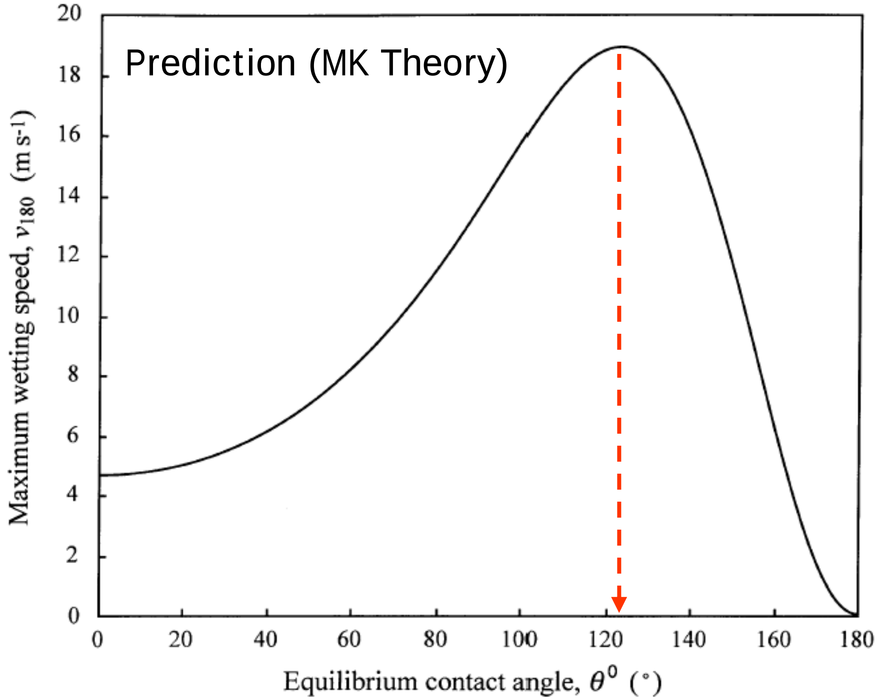
$$u = \frac{2hk_S}{\mu\lambda^2}\sinh\frac{\gamma\left(\cos\theta_0 - \cos\theta\right)\lambda^2}{2k_BT}, \qquad k_S = \frac{k_BT}{h}\exp\left(-\frac{\Delta G_S}{k_BT}\right)$$



$$-\Delta G_S \cong W_A A = \gamma\left(1+\cos\theta_0\right)\lambda^2$$

Blake (1993)

Optimum Wettability for Coating



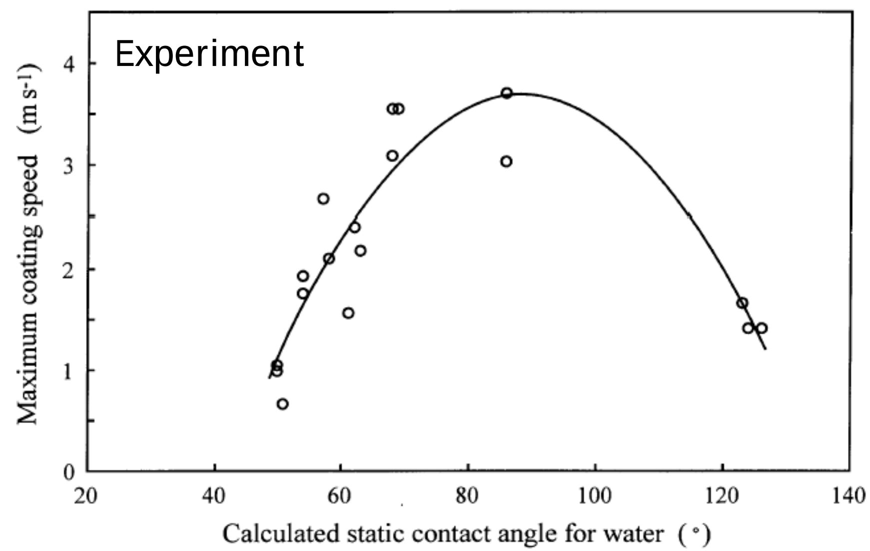
As the static contact angle increases:

- the driving force decreases;
- the molecular friction decreases.

Therefore an optimum static wettability exists.

Experimental evidence supports this prediction.

Prediction is made for water on PET (λ = 3.6 Å). Experiments were carried on dried coatings of aqueous gelatine containing various surfactants (in order to vary the static contact angle).



Blake & de Coninck (2002)